Colour Centres in 2-D hexagonal Boron Nitride

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Declaration of Authorship

I certify that the work in this thesis has not previously been submitted for a degree nor has it been submitted as part of requirements for a degree except as part of the collaborative doctoral degree and/or fully acknowledged within the text. I also certify that the thesis has been written by me. Any help that I have received in my research work and the preparation of the thesis itself has been acknowledged. In addition, I certify that all information sources and literature used are indicated in the thesis. This research is supported by Australian Government research training programme.

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Abstract

Point defects in semiconductors show a rich spin and optoelectronic physics that can be exploited to fabricate qubits for quantum computing technology as well as for single photon sources for quantum cryptography. This thesis contains a detailed study of emission from point defects in hexagonal boron nitride using density functional theory (DFT) and quantum chemistry approaches with an objective to identify the source of observed single photon emission. A survey of possible defects responsible for observed emission is performed using computationally inexpensive generalized-gradient approximation (GGA), Perdew-Burke-Ernzerhof (PBE) and those defects that form localized states with an energy gap of $\sim$2 eV are picked for calculations using highly non-local Heyd-Scuseria-Ernzerhof hybrid functional (HSE06). The photoluminescence line shape is calculated and compared with experiment to propose the most likely defects causing the observed emission. The standard DFT approaches are found to be inaccurate when compared with ab initio CCSD(T), EOM-CCSD, and CASPT2 approaches in predicting the excited-state energies, especially when dealing with states which have considerable open shell character. Thus, a benchmarking scheme is proposed and correction factors are devised for DFT energies. Finally, limitations of the finite model compound used in ab initio calculations are discussed and a possible solution is presented. A complete optical cycle of the likely defects is predicted using results from the HSE06 DFT approach, that are corrected by applying results from the high-level ab initio calculations. Finally, group theoretical analysis of defects is performed and possible applications in quantum computation technology are proposed.

Division of thesis

The division of this thesis is as follows. In Chapter 1, the overall theme of this work and how different concepts fit together is presented. In Chapter 2, the relevant experimental and theoretical literature is reviewed regarding the properties of emitters in h-BN and the context of the present work is presented in detail. In Chapter 3, the computational methods used in this thesis are presented. Chapter 4 contains the results for a survey of different possible emitting centres in h-BN. In Chapter 5, hyperfine coupling parameters are presented and comparisons are made with the experiments. Chapter 6 discusses inaccuracies in DFT energies and compares the calculated energies with ab initio CCSD(T), EOM-CCSD, and CASPT2 approaches. Correction factors for the DFT calculations are also proposed. Chapter 7 contains a study of the spectroscopy of likely defects responsible for the emission from h-BN using the DFT (HSE06) results, after applying correction factors devised in Chapter 6. and proposed optical cycles of the defects. The calculated photoluminescence line shapes for selected transitions are also presented. Polarization of allowed transitions are identified along with spin-orbit coupling driving non-radiative transitions. Zero-field splitting parameters are also presented and potential applications of the studied emitters in quantum applications proposed. Finally, a brief summary of the outcomes of this thesis and proposed future studies are presented.

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Lastly, I dedicate the work to one who has never met me but is with me timelessly**…….**

SAJID ALI

List of Publications from this Work

1. **Sajid, A**.; Reimers, J. R.; Ford, M. J., Defect states in hexagonal boron nitride: Assignments of observed properties and prediction of properties relevant to quantum computation. *Physical Review B* **2018,** *97* (6).

2. **{Sajid, A.**; Tawfik, S. A.}[Equal Authors]; Fronzi, M.; Kianinia, M.; Tran, T. T.; Stampfl, C.; Aharonovich, I.; Toth, M.; Ford, M. J., First-principles investigation of quantum emission from hBN defects. *Nanoscale* **2017,** *9* (36), 13575-13582.

3. Reimers, J. R.; **Sajid, A.**; Kobayashi, R.; Ford, M. J., Understanding and Calibrating Density-Functional-Theory Calculations Describing the Energy and Spectroscopy of Defect Sites in Hexagonal Boron Nitride. *Journal of Chemical Theory and Computation* **2018,** *14* (3), 1602-1613.

4. Grosso, G.; Moon, H.; Lienhard, B.; **Sajid, A**.; Efetov, D. K.; Furchi, M. M.; Jarillo-Herrero, P.; Ford, M. J.; Aharonovich, I.; Englund, D., Tunable and high-purity room temperature single-photon emission from atomic defects in hexagonal boron nitride. *Nature Communications* **2017,** *8*.

5. Z. Xu, C. Elbadawi, T. T. Tran, M. Kianinia, X. Li, D. Liu, T. Hoffman, M. A. Nguyen, S. Kim, J. Edgar, X. Wu, L. Song, **Sajid, A.**, M. Ford, M. Toth, and I. Aharonovich, Single photon emission from plasma treated 2D hexagonal boron nitride. *Nanoscale* **2018,** *10* (17), 7957-7965.

6. **Sajid, A.**; Reimers, J. R.; Kobayashi, R.; and Ford, M. J., Improved methods for predicting the properties of defect states in 2D materials, applied to examine the V_NN_B defect in hexagonal boron nitride. *Journal of Chemical Theory and Computation (submitted)*.

7. **Sajid, A.**; Reimers, R.; and Ford, M. J., Single photon emitters in hexagonal Boron Nitride: A review of progress *(in preparation)*.

Other Publications during this time

1. G. Murtaza, **Sajid. A**., M. Rizwan, Y. Takagiwa, H. Kachai, M. Jibran, R. Khenata, S. Bin Omran. First principles study of Mg_2X (X=Si, Ge, Sn, Pb) Elastic, optoelectronic and thermoelectric properties. *Material Science in Semiconductor Processing*, (2015), 40, 429-435.

2. I. Zhu, L. L. C Lem, T. Nguyen, K. Fair, **Sajid. A**., M. J Ford, M. R. Phillips and C. Ton-That, Indirect excitons in hydrogen-doped ZnO. *Journal of Physics D: Applied Physics 2017*, 50.

3. **Sajid A**, Opto-Electronic Properties of Li_2C_2 Polymorphs. *Madridge J Nano Tech*. 2017, 2(1), 74-76.

4. Munir T, Munir HS, Kashif M, Fakhar-E-Alam M, Shahzad A, Amin N, **Sajid. A.**, Umair M., Synthesis and characterization of Copper Oxide nanoparticles by solution evaporation method. *Optoelectronics and Advanced Materials.* 01 May 2017, 19(5-6), 417-423.

5. M. Azizar Rahman, **Sajid. A.**, A. Gentle, Matthew R. Phillips, Michael J. Ford, Cuong Ton-That Wavelength tunable light source in individual ZnO microrod by Ga incorporation*(submitted)*.

Major Conference Presentations

1. **Sajid, A.**; Reimers, R.; and Ford, M. J. "Defect states in hexagonal boron nitride: Assignments of observed properties and prediction of properties relevant to quantum computation", *ICONN*, 29th January – 2nd February, 2018, Wollongong, Australia.

2. **Sajid, A.**; Reimers, R.; and Ford, M. J., "Emission from Point defect in Hexagonal Boron Nitride", 19th World Congress on Materials Science and Engineering, June 11-13, 2018, Barcelona, Spain.

3. **Sajid, A.**; Reimers, R.; and Ford, M. J., **"**Single photon emission from Hexagonal Boron Nitride", *ISHHC18*, July 22-25, 2018, Sydney, Australia.

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